

OCT 17

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Via Express Mail

Gwen Zervas
Case Manager
Bureau of Federal Case Management
Department of Environmental Protection
401 East State Street (CN-028)
Trenton NJ, 08625

Re: Transmittal of additional Work Plan for Bench Scale
Fenton's Reagent testing, L.E. Carpenter Superfund Site,
Wharton, New Jersey.

Dear Ms. Zervas:

As per my letter of October 6, 2000, here is the second, and
final work plan for the Fenton's Reagent testing, that might
be used to supplement efforts being considered at the L. E.
Carpenter site. I hope you find it helpful.

Once again, thank you for the opportunity to review and
provide comments. Please feel free to contact me to discuss
this matter further at (212) 637-4411.

Yours truly,

Stephen Cipot

cc: Carole Petersen, chief (w/o copies)
MaryAnne Rosa, chief (w/o copies)
Andy Crossland, PSB (w/o copies)

bcc: Stephen Cipot, SNRJS (w/copy)

enclosure

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1. INTRODUCTION

Environ Corporation (Environ) has identified an underground discharge of organic compounds (primarily chlorinated hydrocarbons) in soil and groundwater at the Chemical Leaman site in Bridgeport, New Jersey. Based upon a preliminary review of site characterization data provided by Environ, Geo-Cleanse International, Inc. (GCI) believes that geologic and hydrogeologic conditions at the site are amenable to treatment of the known organic contamination by the Geo-Cleanse® Process. The Geo-Cleanse® Process is an in-situ technology to inject hydrogen peroxide and ferrous iron catalyst solutions (Fenton's reagent) to the subsurface to oxidize hydrocarbon organic contaminants to substituent carbon dioxide and water (see Section 2).

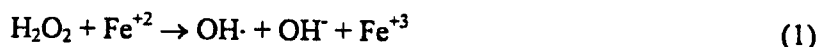
Fenton's reagent oxidation of organic compounds in water and wastewater is well known. The Geo-Cleanse® Process has previously been applied to soil and groundwater for treatment of sites impacted by petroleum hydrocarbons (including polynuclear aromatic hydrocarbons), chlorinated solvents, and many other compounds, including compounds reported by Environ at the Chemical Leaman site. Prior to a field demonstration test, bench scale treatability tests were proposed to evaluate potential effect of site-specific soil and groundwater conditions on overall reaction efficiency, and demonstrate effectiveness of the Geo-Cleanse® Process on contaminants specifically present at the Chemical Leaman site in native soil materials.

The purposes of this document are to:

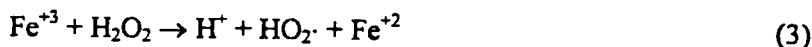
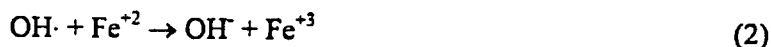
- Describe the fundamental basis of the Geo-Cleanse® Process.
- Describe the objectives and methods of the bench scale autoclave treatability tests to be conducted with Geo-Cleanse® reagents on native soil from the Chemical Leaman site.

2. FUNDAMENTALS OF THE GEO-CLEANSE® PROCESS AND FENTON'S REAGENT

The Geo-Cleanse® Process is a patented, in-situ chemical oxidation technology intended to reduce organic contaminant concentrations in soil and groundwater. The Geo-Cleanse® Process is an aggressive, pressurized injection of concentrated hydrogen peroxide and ferrous iron catalyst, which together are known as Fenton's reagent and generate a hydroxyl free radical that acts as the active oxidizing agent (Fenton, 1894; Haber and Weiss, 1934). The basic radical-producing reaction is characterized as:



where H_2O_2 is hydrogen peroxide, Fe^{+2} is ferrous iron, $\text{OH}\cdot$ is hydroxyl free radical, OH^- is hydroxyl ion, and Fe^{+3} is ferric iron. Fenton's reagent chemistry is complex, involving a number of additional reactions producing both oxidants and reductants that contribute to contaminant destruction (e.g., Watts et al., 1999):

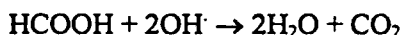
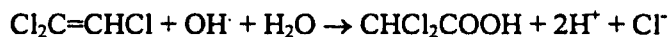


where $\text{HO}_2\cdot$ is hydroperoxyl radical, HO_2^- is hydroperoxyl anion, O_2 is molecular oxygen, H^+ is hydronium ion, and H_2O is water. Additional reactions occur with organic compounds. The suite of reactions associated with Fenton's reagent is complex, but very effective at destroying many organic compounds dissolved in groundwater, sorbed to soil particles, or existing as non-aqueous phase liquids in subsurface environments.

The hydroxyl free radical generated by Fenton's reagent is a powerful, non-selective oxidant. Oxidation of an organic compound by Fenton's reagent is rapid and exothermic (heat-producing). Rate constants for reactions of hydroxyl free radicals with common environmental pollutants are

typically in the range of 10^7 to $10^{10} \text{ M}^{-1}\text{s}^{-1}$ (e.g., Buxton et al., 1988; Haag and Yao, 1992) and 100% mineralization is complete in minutes.

Site characterization data provided by Environ indicate that the primary organic contaminants present at the site are chlorinated solvents, including trichloroethene (TCE) and its natural degradation products cis-1,2-dichloroethene (CIS) and vinyl chloride (VC). Fenton's reagent oxidizes chlorinated aliphatic compounds such as TCE and its natural degradation products to substituent carbon dioxide, water, and chloride, via an oxidation pathway that involves carboxylic acids. The oxidation pathway is not a dehalogenation process like natural biodegradation, and additional CIS or VC is not produced by Fenton's reagent oxidation. Reported rate constants for reaction of OH^\cdot with TCE range from $4.0\text{--}4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Buxton et al., 1988), indicating an extremely rapid reaction. Oxidation of TCE ($\text{Cl}_2\text{C}=\text{CHCl}$) by Fenton's reagent produces dichloroacetic acid (CHCl_2COOH) as the only significant intermediate product, which is further oxidized to formic acid (HCOOH) and finally to water (H_2O), carbon dioxide (CO_2), and chloride (Cl^-) (Figure 1):



Fenton's reagent effectively and completely oxidizes TCE and its related compounds to stoichiometric quantities of carbon dioxide, water, and chloride in soil and groundwater under laboratory-simulated conditions (e.g., Ravikumar and Gurol, 1994; Gates and Siegrist, 1995) and in GCI field experience (e.g., Bryant and Wilson, 1998, 1999; Levin et al., 2000; Maughon et al., 2000).

Site characterization data provided by Environ also indicate that petroleum hydrocarbons are present at the site, including benzene, toluene, ethylbenzene and xylenes (cumulatively referred to as BTEX) and polycyclic aromatic hydrocarbons (PAHs). The structure of each of these compounds is similar in that all are composed of one or more benzene-type (aromatic) ring structures. The oxidation pathway of benzene is well known (Merz and Waters, 1949; Lindsay Smith and Norman, 1963; Walling and Johnson, 1975; Edwards and Curci, 1992; Scheck and Frimmel, 1995) and provides a model for the oxidation pathway of other BTEX and PAH compounds. The rate constant for oxidation of benzene by hydroxyl free radicals is reported as $7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Buxton et al., 1988). Reaction of benzene with hydroxyl free radicals produces short-lived and highly reactive aromatic intermediates. The initial attack is hydroxylation to phenol and subsequent oxidation to orthobenzoquinone (Figure 2). Once orthobenzoquinone is formed, ring tension and oxidizing agents

rapidly force fission of the aromatic ring to produce muconic acid, a linear carboxylic acid. The pathway then proceeds through a series of intermediate carboxylic acids to carbon dioxide. Hydroxyl radicals do not readily oxidize certain carboxylic acids produced as intermediate oxidation products from organic compounds, thus mineralization may be incomplete although no hazardous intermediate compounds are formed. For example, oxalic acid produced as an intermediate product of Fenton's reagent oxidation of benzene is not readily oxidized in the absence of light (e.g., Karpel vel Leitner, 1997).

A similar series of intermediate products, possibly also including benzoic acid, is also reported for toluene (Merz and Waters, 1949; Lindsay Smith and Norman, 1963; Walling and Johnson, 1975). Although the oxidation pathways for other compounds, particularly PAH compounds, are not as well known as for benzene, the susceptibility of the remaining BTEX and PAH compounds to Fenton's reagent oxidation is well demonstrated (e.g., Martens and Frankenberger, 1995; Chen and Pignatello, 1997; Lindsey and Tarr, 2000).

3. BENCH TEST GOALS AND LIMITATIONS

Prior to a field test of the Geo-Cleanse process at the Chemical Leaman site, bench scale treatability tests were proposed with the following objectives:

- Evaluate potential effects of site-specific soil and groundwater conditions on overall reaction efficiency.
- Demonstrate the effectiveness of the Geo-Cleanse® Process on targeted organic contaminants identified in soil and groundwater at the Chemical Leaman site.
- Evaluate potential effects of treatment on the concentration of metals in groundwater.

The goal for the bench scale autoclave test is not to reduce the organic compounds present to non-detectable levels. Rather, an oxidation goal of approximately 50-75% is desired so that the reaction and oxidation efficiency can be evaluated.

Use of an autoclave imposes an important limitation on estimating hydrogen peroxide requirements. The autoclave experiments routinely overestimate hydrogen peroxide requirements (relative to requirements observed in the field) by approximately an order of magnitude. The reason is that the tests are conducted on a saturated soil sample, thus injected liquid reagents mix with and displace pore water, generating a "leachate" which is periodically removed from the test vessel as the test progresses. This leachate will contain hydrogen peroxide and as a result, a significant fraction of the hydrogen peroxide introduced to the autoclave is leached out and removed prior to reaction with the soil inside the autoclave. In the field, however, such leachate would not be removed from the system but rather would distribute through the formation to establish the radius of influence for the treatment process.

4. MATERIALS AND METHODS

4.1. Materials

Environ personnel will collect representative saturated soil samples at the Chemical Leaman site from the impacted aquifer horizons that may be targeted during pilot- or full-scale field treatment. Specifically, one sample representative of the sand and one sample representative of the clay materials will be collected. The samples will be submitted blind to GCI (i.e., the locations will not be identified). Approximately 1 gallon of soil from each of two locations will be collected by split spoon sampler. The soil samples will be quickly homogenized in the field, packed into a Ziploc®-type resealable plastic bag placed inside a new (previously unused) resealable metal container, and sealed. In addition, 1 liter of groundwater from the site will be collected by bailer or pump and transferred to a 1-L amber glass bottle without headspace. The soil and water samples will not be preserved in any way except for refrigeration. The solid and aqueous samples will be placed on ice and shipped directly to the laboratory for bench testing. Appropriate chain-of-custody and handling protocols will be followed.

4.2. Methods

Bench test experiments will be conducted at GCI's laboratory. Laboratory facilities at GCI include a dedicated fume hood, refrigerated sample storage, a Hach DR-2010 data logging spectrophotometer, micropipettors, glass electrode pH meters, thermometers, analytical balances, reagents, and all associated glassware and other facilities necessary for proper cleaning, storage, sampling, analyses and other experimental procedures required for these tests.

All laboratory materials to which the samples or reagents may come into contact will be composed of Pyrex, stainless steel, Teflon, or polyethylene (as dictated by the analytical procedure), and will be cleaned with deionized water and Alconox and then triple-rinsed with deionized water prior to use. Solution volumes will be measured with class A graduated cylinders, volumetric flasks or a calibrated micropipettor. Sample or reagent masses will be measured with calibrated analytical balances. Solution pH will be measured to 0.01 pH units with a glass electrode meter calibrated daily unless hydrogen peroxide is detected in the sample. If hydrogen peroxide is detected, pH will be measured with pH strips (range 0 to 6) because hydrogen peroxide will damage the pH electrode. All reagents are reagent grade or better, and only deionized water will be used in all experiments.

The chemical oxidation experiments will be conducted in an autoclave, a sealed vessel that allows for experiments to be conducted at elevated temperatures and pressures intended to simulate

in-situ chemical oxidation conditions. This system also provides control and quantification of all inputs and outputs of fluids and gases from the experiment, which allows for calculation of a complete mass balance to estimate oxidation efficiency. Two identical autoclaves will be used to conduct both experiments simultaneously. The interior of the autoclaves is coated with Teflon and fittings are sealed with Viton O-rings. The autoclaves (Figure 3) have a 2-liter volume. Three ports are installed at the top of the autoclave. Reagents are introduced to the autoclave via a rate-controlled dual-feed chemical metering pump, via a perforated ¼-inch diameter stainless steel tube inserted approximately ¾ into the sample. The perforated section is 1-inch in length and covered with 300-mesh stainless steel screen. A temperature probe is inserted through an additional port for constant temperature monitoring. Offgases are vented and monitored through a third top port. The gas venting/monitoring assembly consists of a pressure gauge and two pressure-relief valves. One valve is set to release at 20 pounds per square inch (psi) and is intended for normal offgasing. When the autoclave pressure reaches 20 psi, gases are released and first passed through a water trap to collect any vented liquids, then through dehydrated silica gel to trap water vapor and organics, and finally through an activated carbon filter to trap organic compounds that pass through the silica gel trap. The pressure relief valve is spring actuated and thus opens and closes slowly. The second pressure-relief valve is set at 60 psi and is intended only for emergency pressure relief. A port at the bottom of the autoclave is used to periodically drain leachate.

Each autoclave is loaded with approximately 3 kg of homogenized soil and then sealed. An approximately ¼- to ½-inch headspace is packed with nylon filter material to prevent solids from clogging the gas vent and pressure ports. Pre-treatment soil samples are collected for each experiment while loading the autoclave, so that the pre-test baseline samples are representative of the soils placed in the autoclave. All samples are stored in a refrigerator (4°C) until shipment to an analytical laboratory. The carbon filter and silica gel masses are then measured and loaded into the traps. Reagents are prepared and the experiments are begun.

The injection will be cycled between catalyst and hydrogen peroxide because the reagents cannot be injected simultaneously to the autoclave. Pressure and temperature will be monitored continuously and recorded at approximately 15-minute intervals. Ambient room temperatures are approximately 72°F. Reaction temperatures are typically maintained between 90° and 100°F. Pressure will be maintained at approximately 20 to 25 psi using the pressure relief valve vented through the silica gel and carbon filter. These pressure and temperature ranges are similar to those anticipated during a Geo-Cleanse® field treatment program. Gas samples will be collected and analyzed at approximately 15-minute intervals (if gas is being produced) for carbon dioxide, oxygen and volatile

organic compounds (using a photoionization detector). Leachate will be collected periodically (as required to release liquids from the autoclave) and the cumulative volume recorded after each collection event. Accumulated leachate will be stored for sampling upon completion of the bench test.

The test will be conducted over a period of approximately 5 days. A catalyst solution with approximately 100 ppm of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and a pH of 4 (established with dilute sulfuric acid) will be added first to establish appropriate conditions, if needed. Leachate pH will be periodically monitored to determine when a mildly acidic pH (<6) has been achieved inside the autoclave. Hydrogen peroxide addition will then begin. Leachate pH monitoring during the test will determine if and when additional catalyst will be added, but typically catalyst is added at the beginning, middle and end of each day. The volume of catalyst added to the autoclave will be recorded and reported as part of the monitoring data.

Because of the high level of contamination anticipated in the soil samples, the injection will be initiated with 6.25% hydrogen peroxide solution in order to begin the test with a less vigorous reaction and to allow detailed monitoring. Typical hydrogen peroxide injection rates are approximately 5 mL per minute, or as necessary to achieve and maintain the target temperature and pressure. The autoclave may be warmed with a heat tape, or injection rate decreased, if necessary to assist with temperature regulation. Injection will continue until significant hydrogen peroxide (>100 mg/L) is detected in the leachate, at which time the system will be allowed to react until hydrogen peroxide in the leachate is <100 mg/L. The volume and concentration of hydrogen peroxide will be recorded and reported as part of the monitoring data.

The test will be concluded when, based upon the monitoring parameters, approximately 50 to 75% of the contaminant mass has been destroyed. Evaluation of the destruction range is subjective, but based upon GCI's prior experience this mass reduction has been achieved when carbon dioxide levels are approximately 1% or less, oxygen levels are greater than 30%, and photoionization detector measurements are less than approximately 5 parts per million. At the conclusion of the experiment the total (cumulative) leachate volume will be recorded and a filtered composite sample collected for analysis. A second filtered composite leachate sample will be collected and adjusted with dilute potassium hydroxide to ambient field pH (within ± 0.2 pH units of the baseline ground water sample pH). Next, the carbon filter and silica gel will be weighed and samples also collected for analysis. Finally, the autoclave will be opened and the treated soil quickly homogenized inside the autoclave using a stainless steel trowel, after which samples will be collected for analysis. All samples will be collected as rapidly as possible and stored in a refrigerator (4°C) until shipment. The samples will be

packed with ice in a cooler and delivered (on the same day as collection) by courier to the analytical laboratory.

Titration tests will also be conducted on the groundwater samples submitted to GCI, in which dilute sulfuric and phosphoric acid solutions (pH ~2) are added incrementally while monitoring pH, to provide a qualitative estimate of the buffering capacity of the groundwater only (in the absence of aquifer solids), and the volume of acid that may be required at the site.

4.3. Number of Samples, Preservation, and Analysis

Samples of the untreated soil, treated soil, silica gel, carbon filter, and leachate (unadjusted and pH adjusted) will be collected and submitted for analysis. Analytes will include volatile organic compounds, target analyte list (TAL) metals, and hexavalent chromium. The numbers of samples per medium and analysis for each medium is listed in Table 1. The sample container details, holding times, and analytical methods for each of the two tests are listed in Table 2. As noted in Table 1, three replicate samples of each pre- and post-test soil sample, the unadjusted leachate sample, silica gel sample, and carbon sample will be collected for VOC analysis to evaluate sample homogeneity and concentration variability. Note that the silica gel and carbon will not be analyzed for TAL metals or hexavalent chromium because TAL metals and hexavalent chromium are not expected to volatilize significantly.

Separate to the samples generated during the bench test, a baseline groundwater sample for TAL metals and hexavalent chromium analysis will be collected in the field by Environ at the same time the soil samples for bench testing are collected, and submitted directly to the analytical laboratory (the baseline TAL metals and hexavalent chromium samples are in addition to the 1-liter groundwater samples that will be submitted to GCI as part of the bench scale testing program). The groundwater sample submitted to GCI will be analyzed for iron, pH, alkalinity, and chloride as part of the titration test.

5. DATA ASSESSMENT

Laboratory bench tests will be conducted to determine if the Geo-Cleanse® Process may provide a cost-effective remedial alternative for treatment of chlorinated and petroleum hydrocarbons in soil and groundwater at the Chemical Leaman Site. The Geo-Cleanse® Process is an in-situ chemical oxidation technology that utilizes a mixture of hydrogen peroxide and ferrous iron (Fenton's reagent) to generate a hydroxyl free radical, which is the active oxidizing agent. The goals of the bench test are to determine if Fenton's reagent can oxidize the contaminants present at the site, if site-specific soil and/or groundwater conditions have a negative effect on treatment, and how treatment may affect dissolved metals concentrations in ground water. If these experiments demonstrate the Geo-Cleanse® Process is effective, then a field pilot test will be pursued. Assessment of the test objectives will be performed as follows.

- One of the objectives of the bench test is to demonstrate that Fenton's reagent chemical oxidation (the basis of the Geo-Cleanse® Process) will oxidize the compounds present in site aquifer materials present at the Chemical Leaman site. To accomplish this goal, the mass and concentration of each VOC target compound will be measured in the untreated soil (the input), treated soil (for residual), leachate, and in the silica gel and carbon trap material (for volatilized fractions). The difference between contaminant mass in the untreated soil, and the cumulative contaminant mass in the treated soil, leachate, and volatilized fractions, represents the oxidized mass. Because the autoclave is a closed system, all inputs and outputs are controlled and measured, thus this system is able to quantitatively determine oxidized mass.
- An additional objective is to evaluate potential effects of soil and groundwater conditions on overall reaction efficiency. In particular, pH of the leachate over the course of the experiment, and carbon dioxide concentration in offgas prior to introduction of hydrogen peroxide (if gas is produced), will be used to determine if solid carbonate minerals in the soil matrix may affect treatment by inhibiting pH adjustment. These measurements will be reported and discussed in the Bench Scale Testing Report.
- A final objective is to evaluate potential effects of treatment on the concentration of metals in groundwater. This will be accomplished by comparing TAL metal and

hexavalent chromium concentrations in pre-test baseline water samples (collected in the field by Environ at the time the soil samples are collected) with post-test leachate samples (both with and without pH adjustment).

6. REPORTING

Verbal updates will be provided as requested by Environ. All observations and data will be recorded in a permanent laboratory notebook. All photographs will be stored in a permanent archive. A Bench Scale Testing Report will be prepared by GCI after receipt of all analytical data. This report will contain a summary of the procedures, volumes and concentrations of injected reagents, vapor and reagent monitoring data, contaminant mass balance calculations, and laboratory analytical data. Conclusions will be drawn regarding the overall effectiveness of the Geo-Cleanse® Process on aquifer soils from the site, possible formation of hazardous intermediate products, and estimated hydrogen peroxide requirements for field treatment. The results of these experiments will be used to develop a field pilot program of the Geo-Cleanse® Process at the Chemical Leaman site.

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TABLE 1. NUMBER OF SAMPLES PER TEST

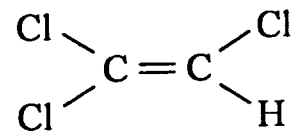
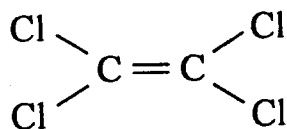
Media	VOCs	TAL Metals / Cr ⁺⁶	Titration / Buffering
Untreated Groundwater	0	1*	1
Untreated Soil	3	1	0
Treated Soil	3	1	0
Leachate	3	1	0
Leachate (pH adjusted)	0	1	0
Silica Gel	3	0	0
Carbon	3	0	0

**Untreated groundwater sample will be collected in the field by Environ for baseline TAL metals*

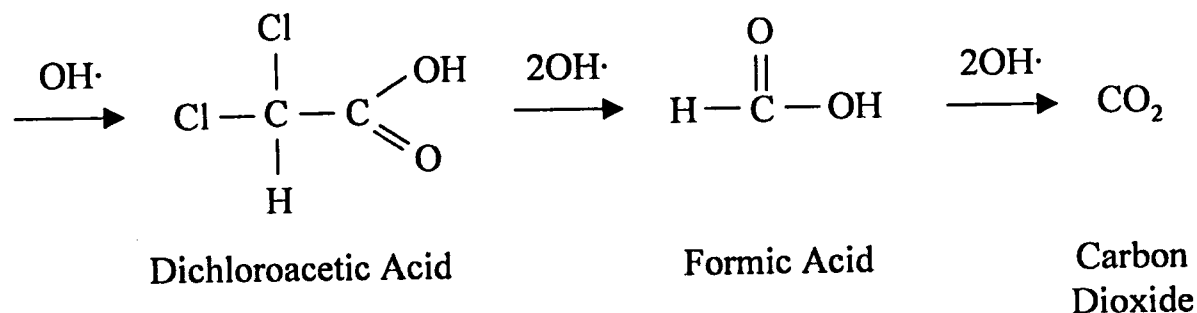
TABLE 2. SAMPLE CONTAINERS, VOLUMES, PRESERVATIVES, METHODS AND HOLDING TIMES

Analysis	Container	Volume	Preservative	SW-846 Determinative Method	Holding Time
<i>Soil/Solid Samples</i>					
VOCs	Glass	4 oz	Cool 4°C	8260B	14 days
TAL Metals	Polyethylene	8 oz	Cool 4°C	6010B; 7471A for Hg	6 months; 28 days for Hg
Hexavalent Chromium	Glass	4 oz	Cool 4°C	3060-7196A	7 days
<i>Aqueous Samples</i>					
VOCs	Glass, teflon-lined septum cap	2 x 40 mL	Cool 4°C, HCl to pH <2	8260B	14 days
TAL Metals	Polyethylene	500 mL	Cool 4°C, HNO ₃ to pH <2	6010B; 7470A for Hg	6 months; 28 days for Hg
Hexavalent Chromium	Glass	500 mL	Cool 4°C	3060-7196A	24 hours

Tetrachloroethene



Trichloroethene

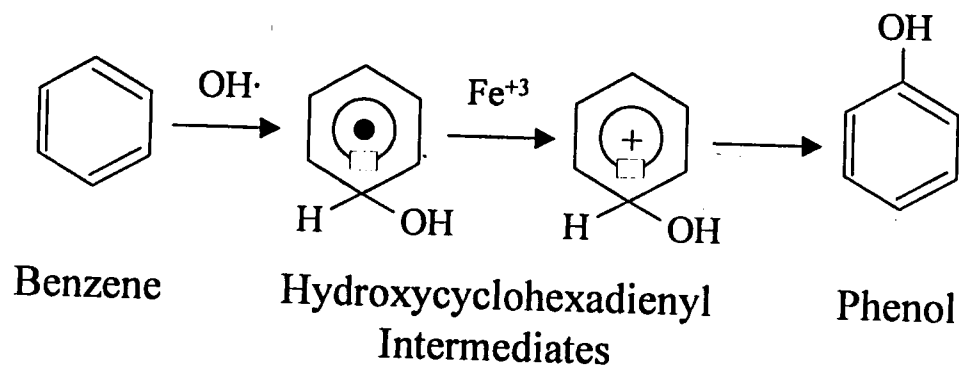


References: Leung et al., 1992; Sato et al., 1993

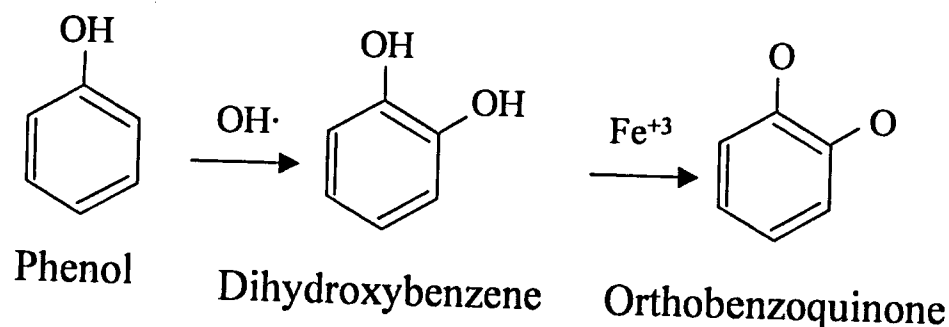
**FIGURE 1. Tetrachloroethene (PCE) and Trichloroethene (TCE)
Oxidation Pathway**

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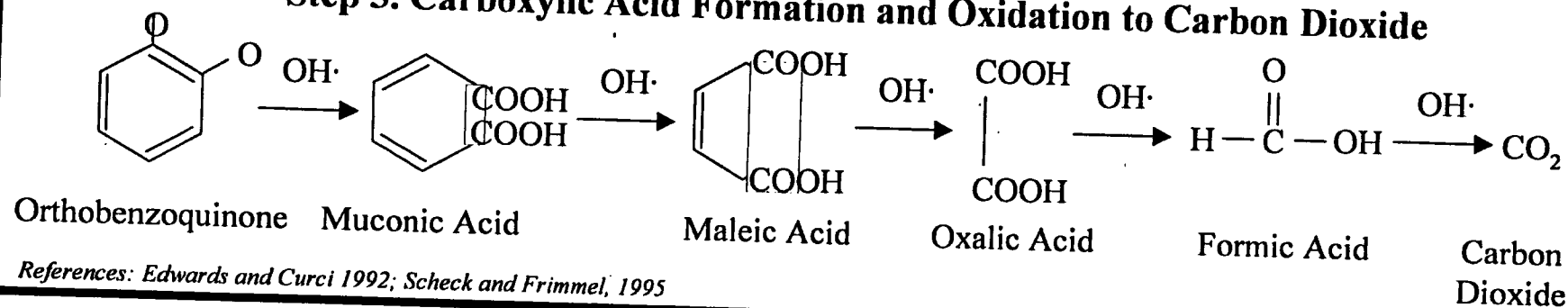
**Step 1.
Benzene
Hydroxylation
to Phenol**



**Step 2.
Phenol
Oxidation to
Benzoquinone**



Step 3. Carboxylic Acid Formation and Oxidation to Carbon Dioxide



References: Edwards and Curci 1992; Scheck and Frimmel, 1995

FIGURE 2. Benzene Oxidation Pathway

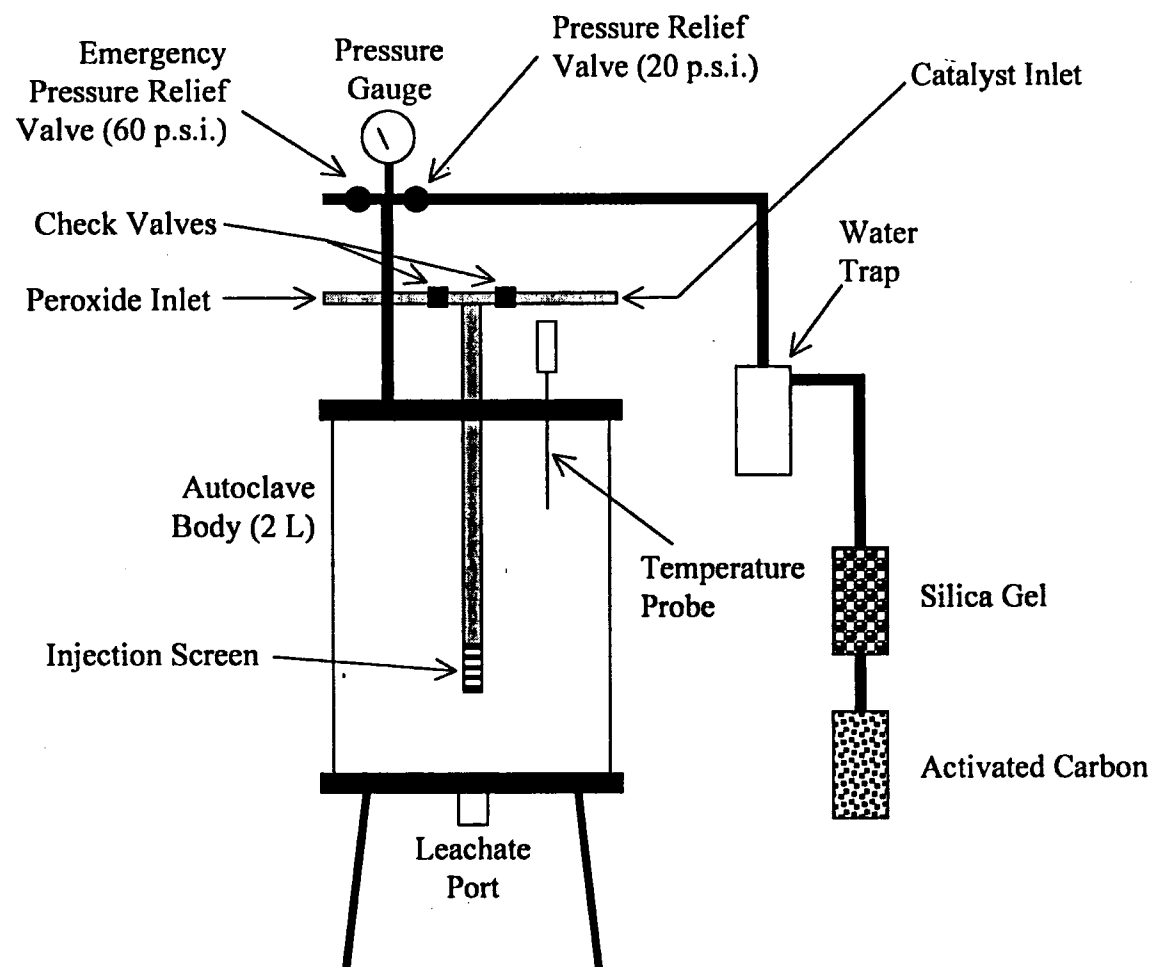


FIGURE 3. Schematic of Geo-Cleanse® Autoclave Bench Test System



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